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STRUCTURE-PROPERTY RELATIONSHIPS FOR OPTIMAL THERMO-MECHANICAL PERFORMANCE IN ORGANIC CYANATE ESTERS

5 February 2013

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Outline



- Background:
 - Balancing T_G , Processing, and Char Yield in Cyanate Esters
 - Different Types of “Thermal” Stability
- Effects of Resin Chemical Structure
 - Network Segment Types
 - Network Junction Types
- Effects of Composition
 - Synergy through Blending



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Cyanate Esters for Next-Generation Aerospace Systems



Glass Transition Temperature
200 – 400 °C (dry)
150 – 300 °C (wet)

Resin Viscosity
Suitable for
Filament
Winding / RTM

Compatible with
Thermoplastic
Tougheners and
Nanoscale
Reinforcements

High T_g

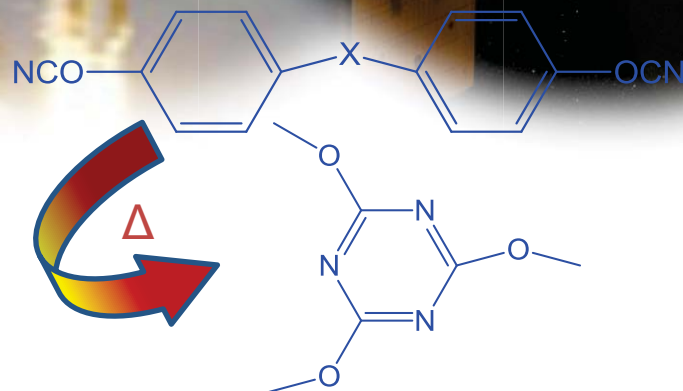
Onset of Weight
Loss:
> 400 °C with High
Char Yield

Ease of
Processing

Resistance to
Harsh
Environments

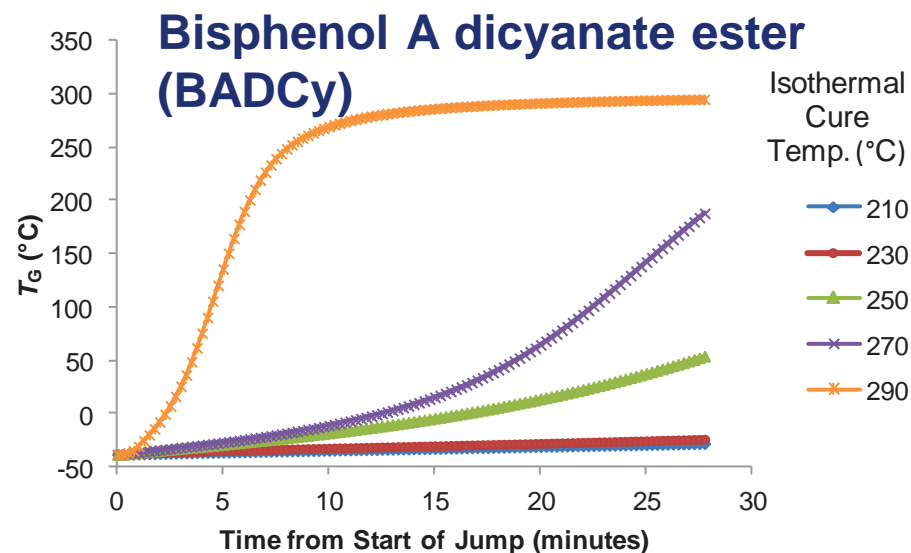
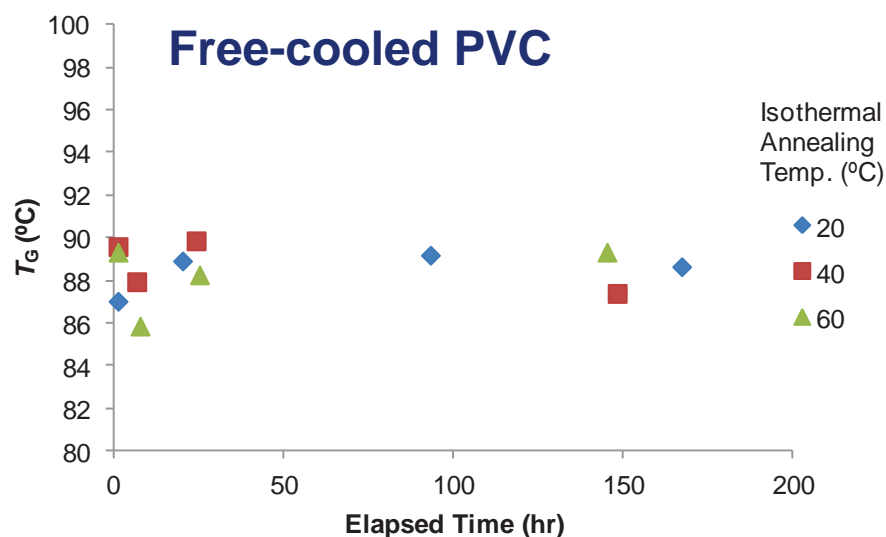
Good Flame,
Smoke, &
Toxicity
Characteristics

Low Water Uptake
with Near Zero
Coefficient of
Hygroscopic
Expansion





Thermosetting Polymers Have a T_g Envelope – Not Just a T_g

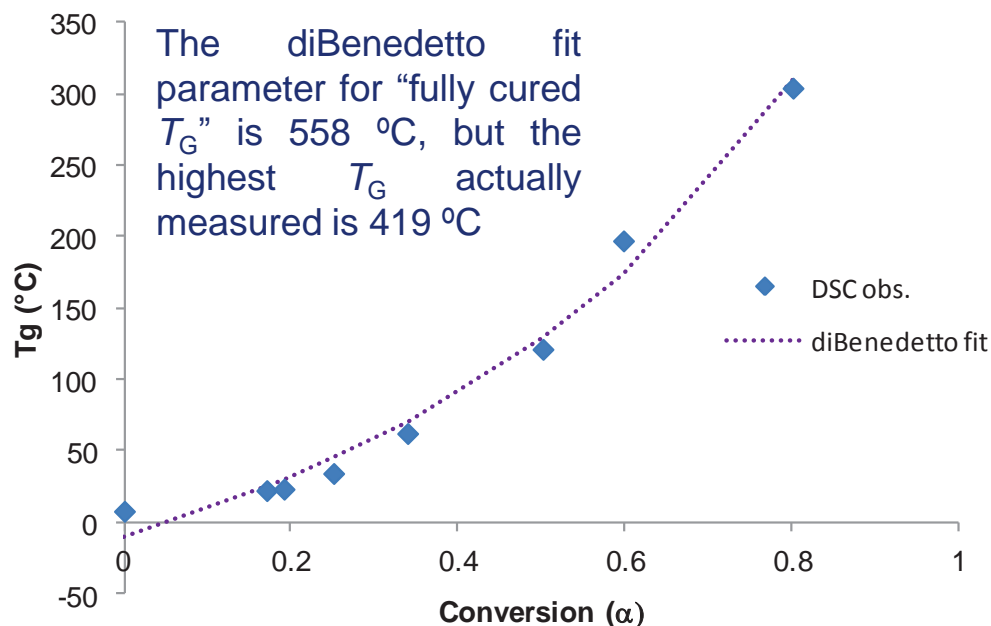


A. R. Berens and I. M. Hodges, *Macromolecules* **1982**, 15, 756 (digitized data from Fig. 2)

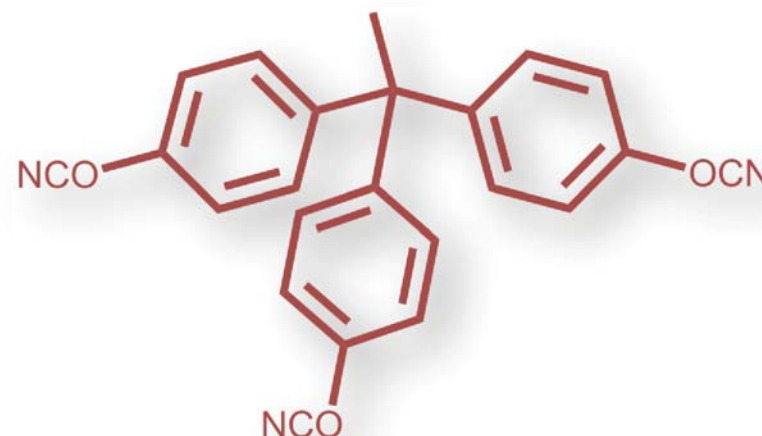
- The glass transition temperature of a thermoplastic such as PVC exhibits a nearly fixed value regardless of processing-induced changes to the system
- In contrast, the glass transition temperature of a thermosetting polymer can vary over a wide range of temperatures depending on how the polymer is processed
- For cyanate esters, the bounds of the T_g envelope are typically well-defined because of the well-defined cure chemistry



The Envelope May Be Unknown – Some Monomers Can Not Cure Fully



“ESR255”

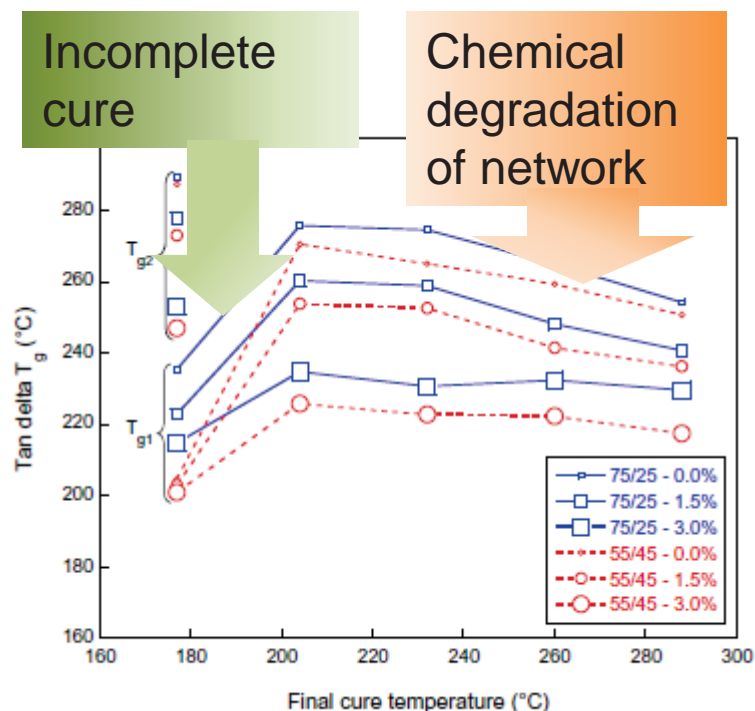


Conversion determined via combined DSC/IR

- Essentially, ESR255 forms such a rigid macromolecular network that the molecular strain energy needed to connect all the loose ends is great enough to break the chemical bonds, so “full cure” simply is not geometrically possible
- Since achieving complete cure is critical for the long-term hydrolytic stability of cyanate esters, a monomer such as ESR255 is actually too rigid by itself
- Even if they can be fully cured, rigid cyanate esters often require very high temperatures and/or active catalysts (which hurt stability) to cure effectively



Thermo-mechanical versus Thermo-chemical Stability



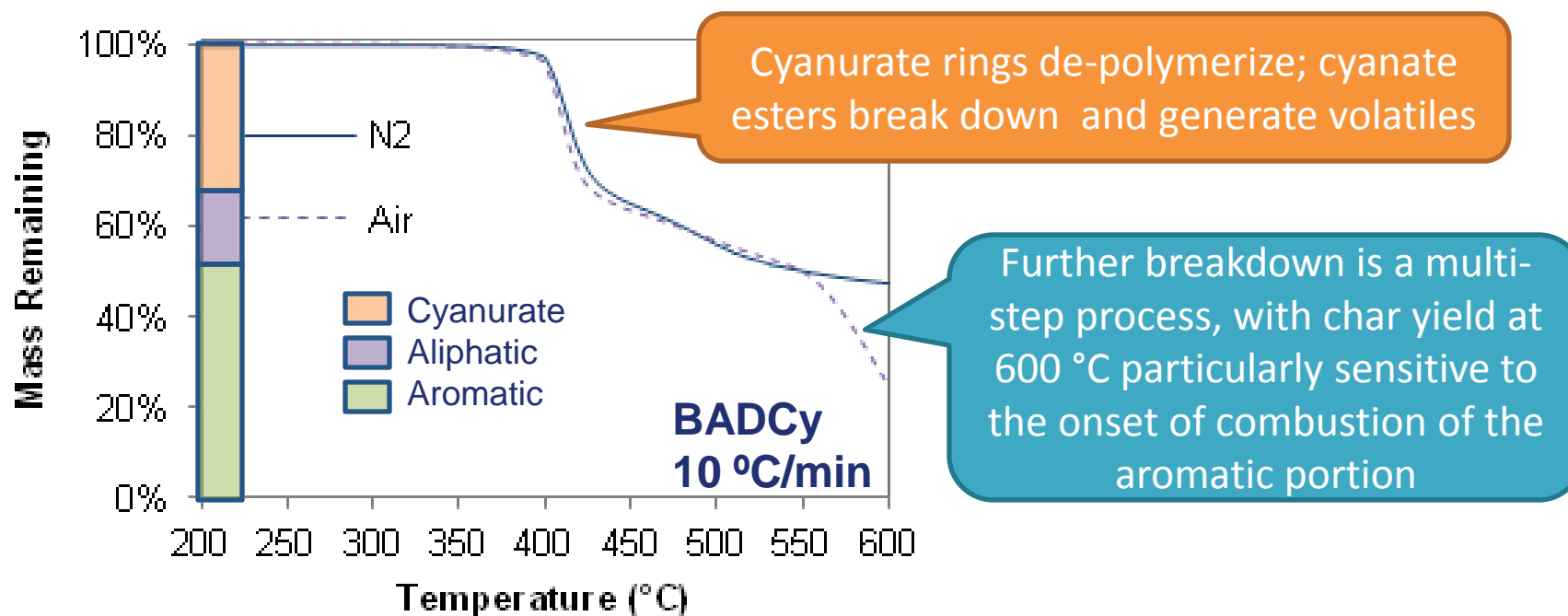
Goertzen, W. K.; Kessler, M. R. *Composites: Part A* **2007** 38, 779–7, Fig. 6, for blends of EX1551 / EX1510 – catalyst.

- The more rigid the network, the higher the thermo-mechanical stability (i.e. softening point for a given network structure).
- Many networks cannot achieve their maximum possible thermo-mechanical stability because at the high temperatures needed for cure, chemical bonds break (i.e. thermochemical stability is limited).
- Typically, adding flexible chemical linkages (such as aliphatic groups) to the chemical structure of a monomer will reduce the rigidity, facilitating the achievement of full cure, but at the expense of thermo-chemical stability.

Needed: a flexible chemical linkage that enables full cure of cyanate esters at acceptable temperature-catalyst combinations while maintaining the desirable chemical degradation characteristics (both rates and char yields) of rigid systems



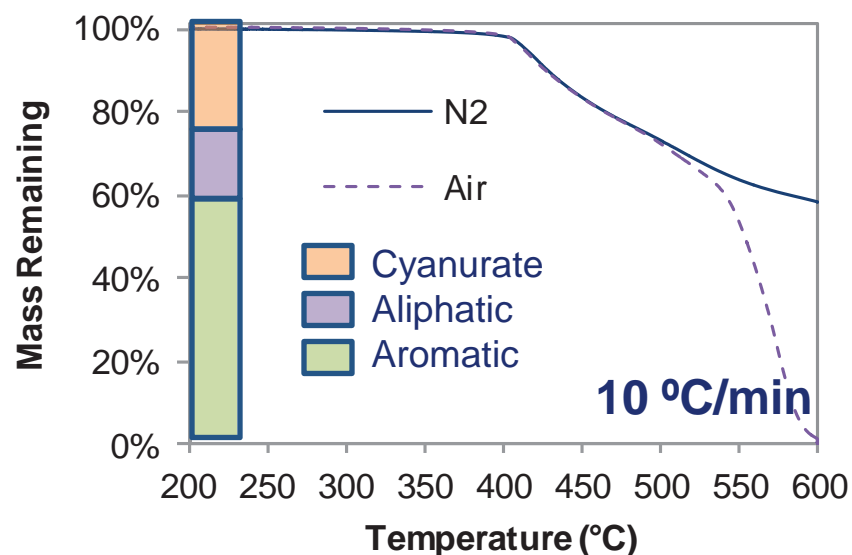
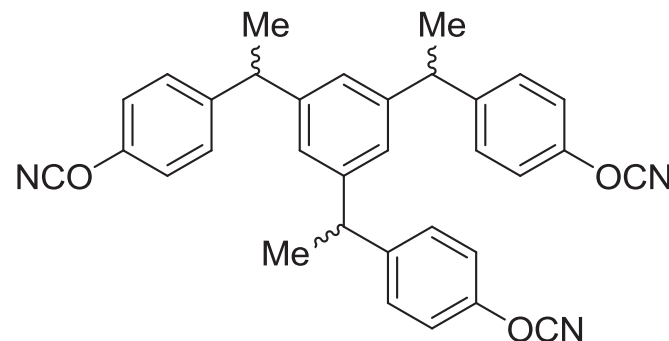
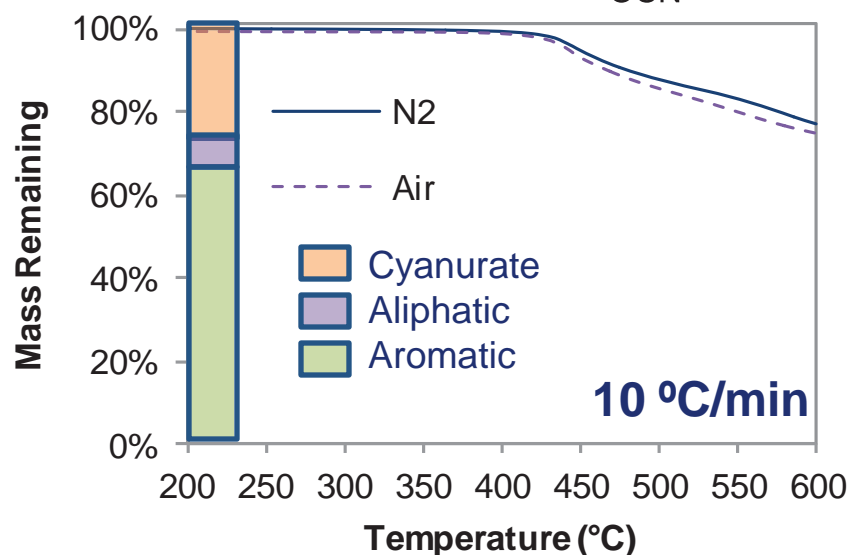
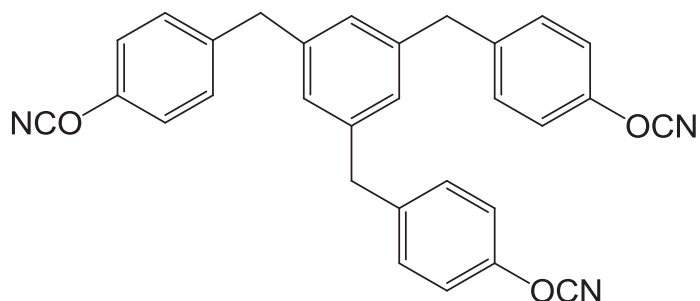
TGA of Cyanate Esters



- TGA provides a simple tool to assess onset temperatures, rates, and char yields associated with the decomposition of cyanate ester networks
- A reasonably slow TGA scan also drives all cyanate ester systems close to the maximum possible extent of conversion (via *in-situ* cure) at the point where decomposition begins



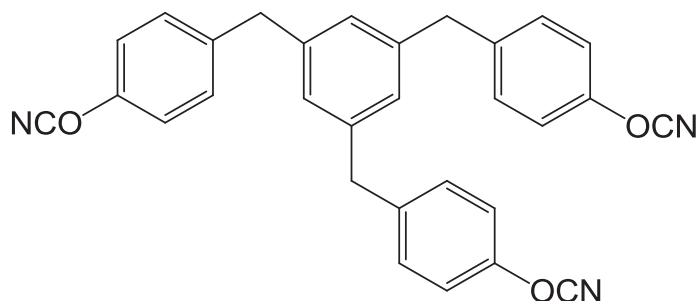
Cyanate Ester TGA: Methylene versus Ethylidene Segments



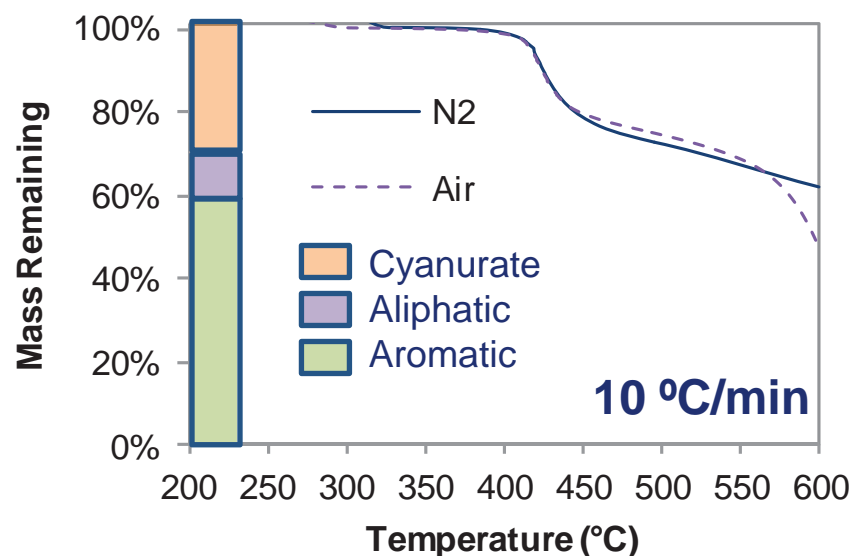
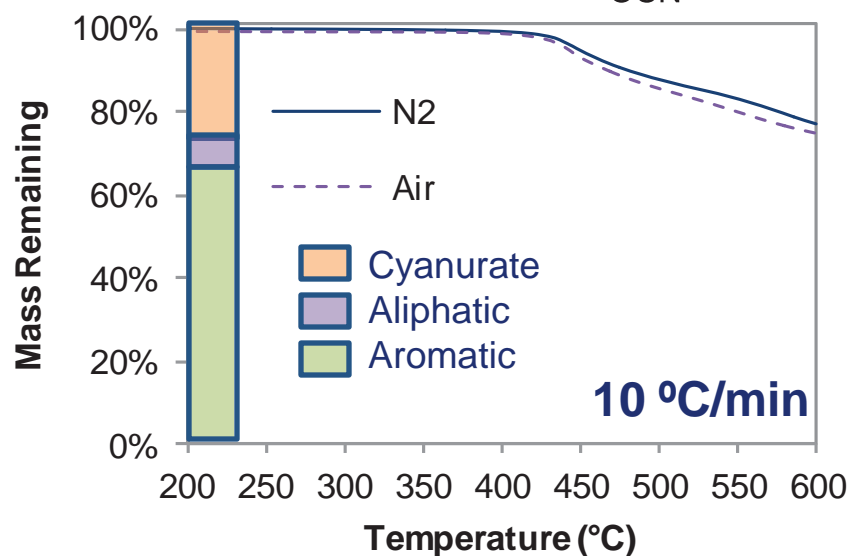
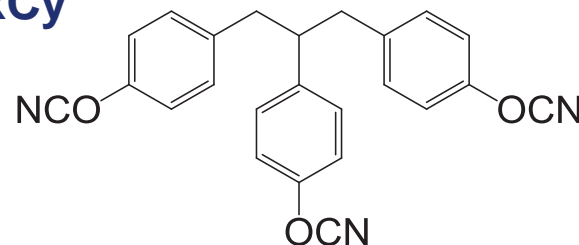
- The tricyanate with methylene segments shows delayed onset of degradation, reduced decomposition rates, and very high char yield
- The tricyanate with ethylidene segments behaves much like BADCy when taking into account the composition, with slightly earlier aromatic combustion



Cyanate Ester TGA: Aliphatic *versus* Aromatic Junctions



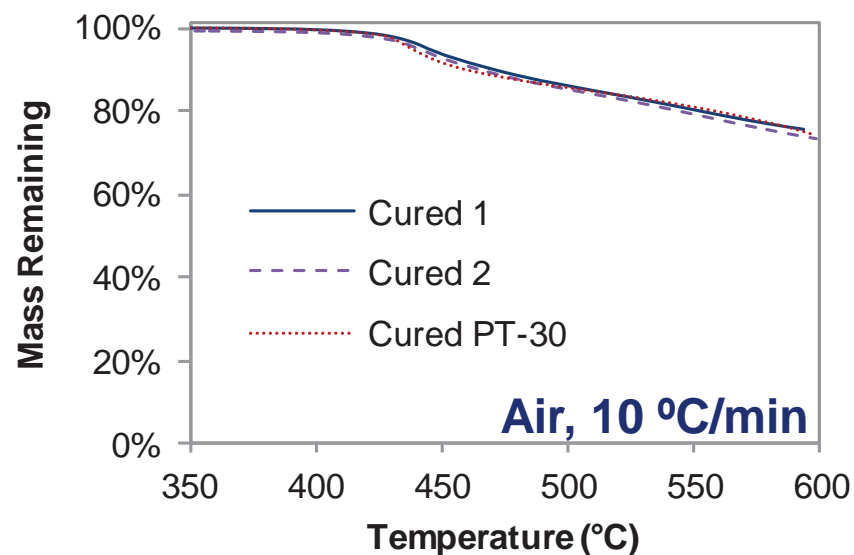
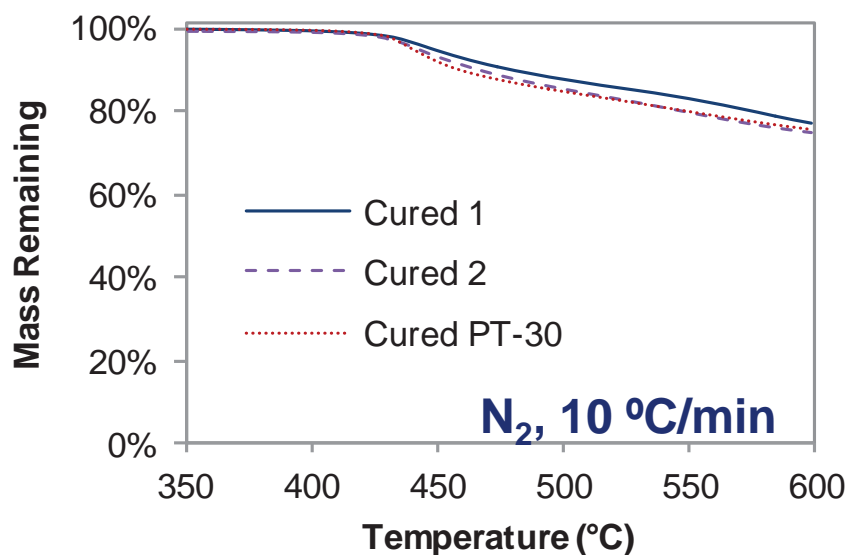
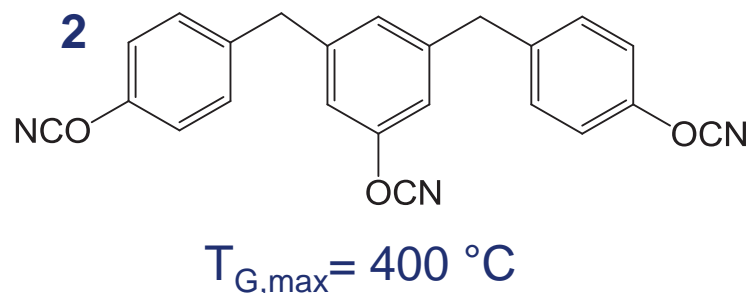
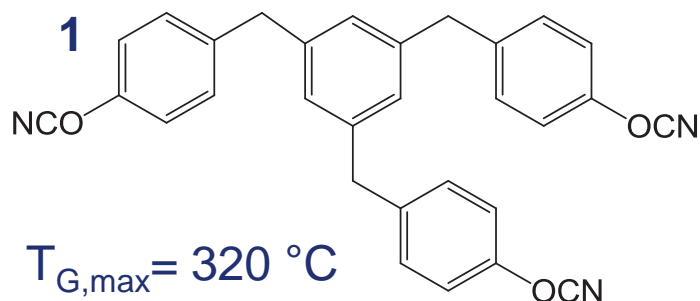
“FlexCy”



- The tricyanate with the aliphatic junction (tertiary carbon) also follows the pattern for BADCy, taking into account composition, with a slightly delayed onset of aromatic combustion compared to BADCy



Segment Flexibility Can Be Tuned Without Affecting Char Yields



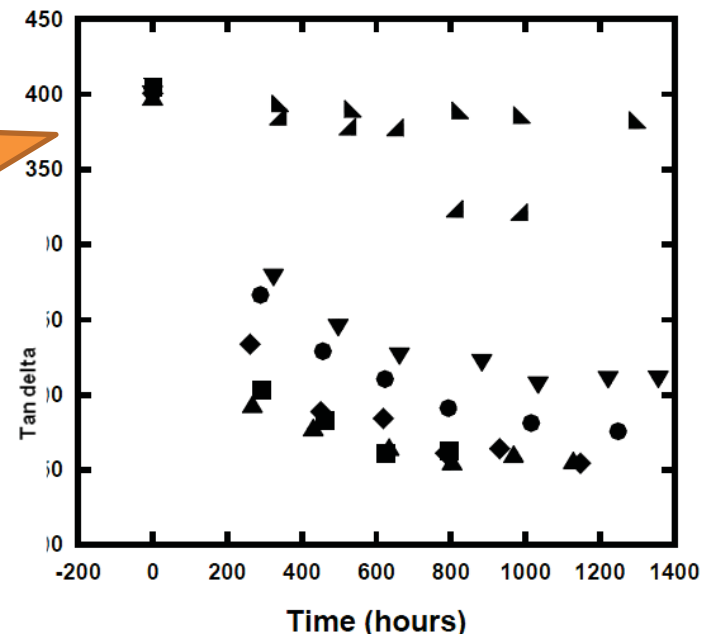
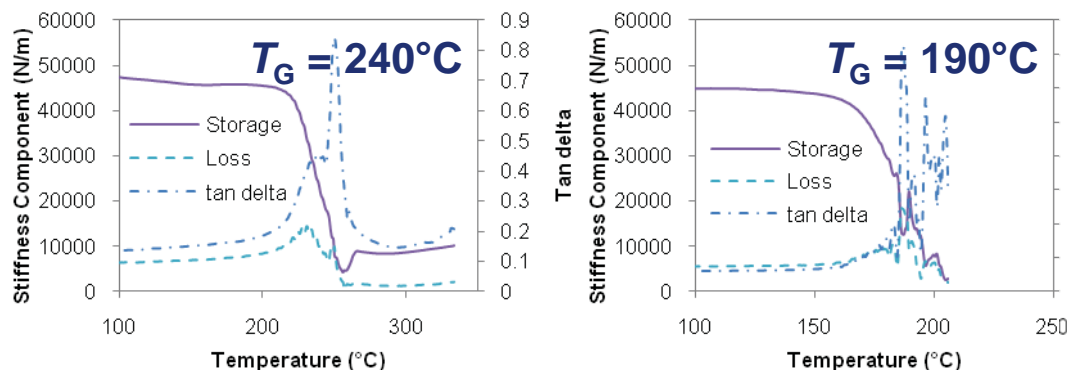
- Note that PT-30 is similar to an oligomeric version of **2**
- Tuneability of $T_{G,max}$ enables full cure to be achieved with a wider range of catalysts under typical processing constraints



From the High Temple Database: Catalysts Control More than Cure



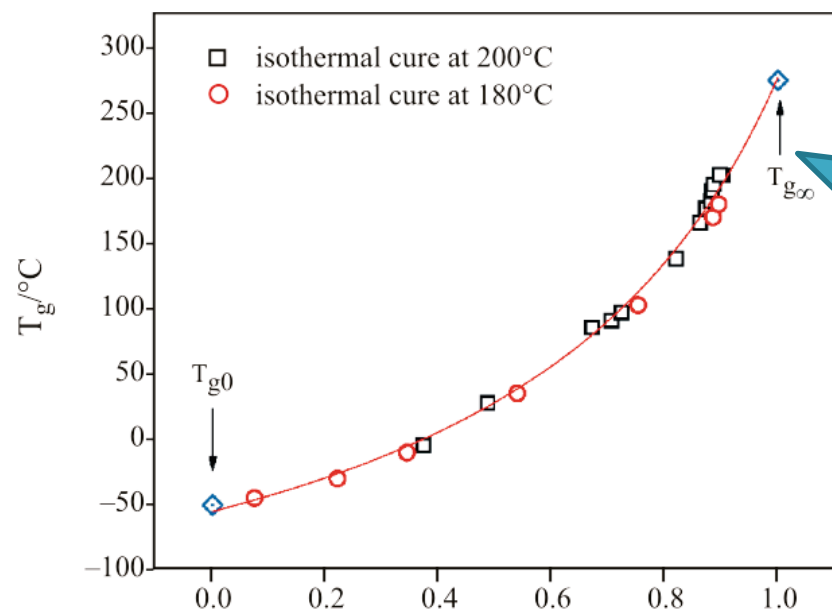
T_G as a function of immersion time in hot water for fully cured PT-30 plaques; originally presented at High Temple 29 by Palmese et al.



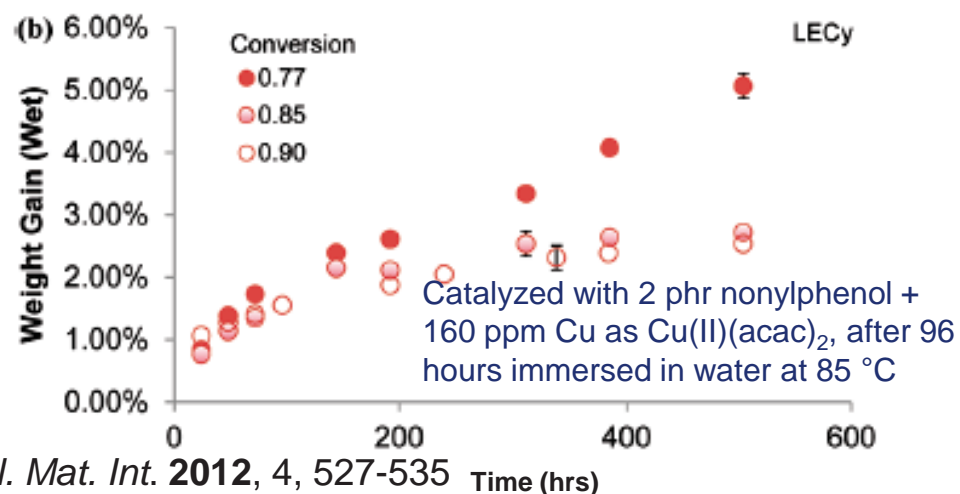
- TMA of Primaset LECY without (left) and with (right) 2 phr nonylphenol + 160 ppm Cu as Cu(II)(acac)_2 , after 96 hours immersed in water at 85°C (first reported at SAMPE Fall 2010)
 - Most types of cyanate ester chemistry, including cure, side reactions, and hydrolytic degradation, are controlled by catalysts
 - The freedom to choose catalysts = the ability to get desirable handling and performance characteristics
- Marella (thesis, Drexel Univ., 2008) compared the effect of numerous catalyst types and loadings on the wet T_G of PT-30



Sometimes It Pays to Use a Resin with a Lower “ T_G ”



To obtain the highest T_G values, the highest conversions must be accessible, requiring either high cure temperatures or aggressive catalysts (which can compromise performance)



from X. Sheng, M. Akinc, and M. R. Kessler, *J. Therm. Anal. Calorim.* **2008**, 93, 77-85 for EX-1510

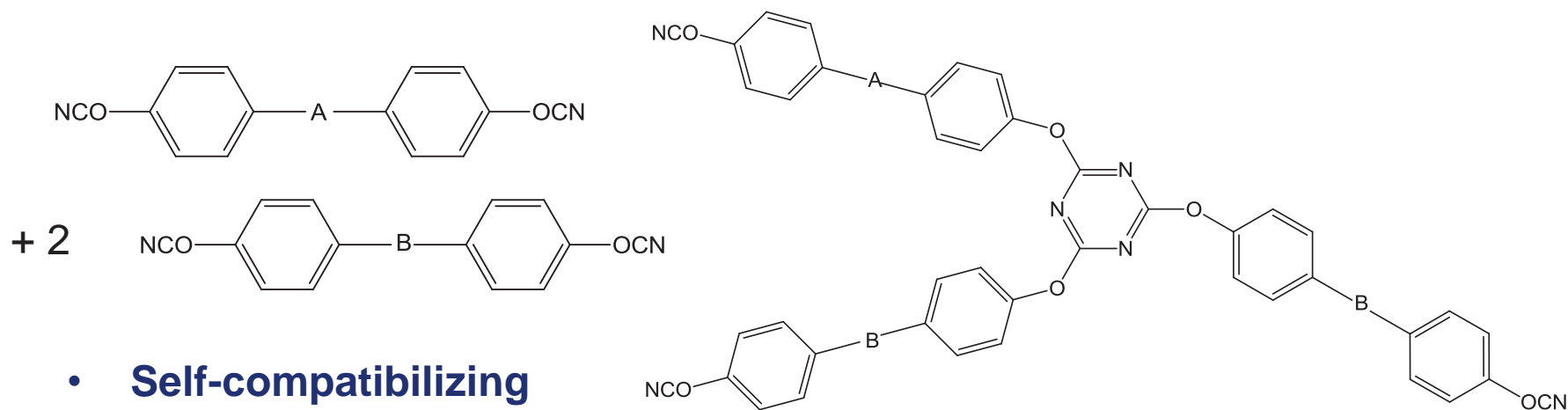
From Reams et al. *ACS Appl. Mat. Int.* **2012**, 4, 527-535

The long-term hydrolytic stability of many cyanate ester resins decreases significantly at lower conversions

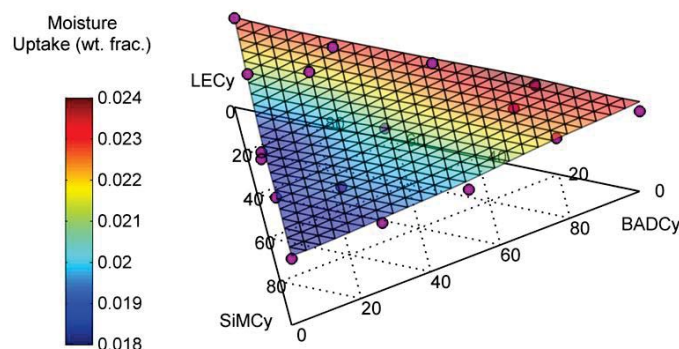
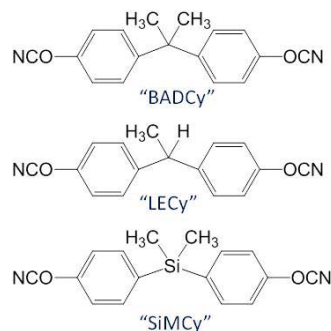
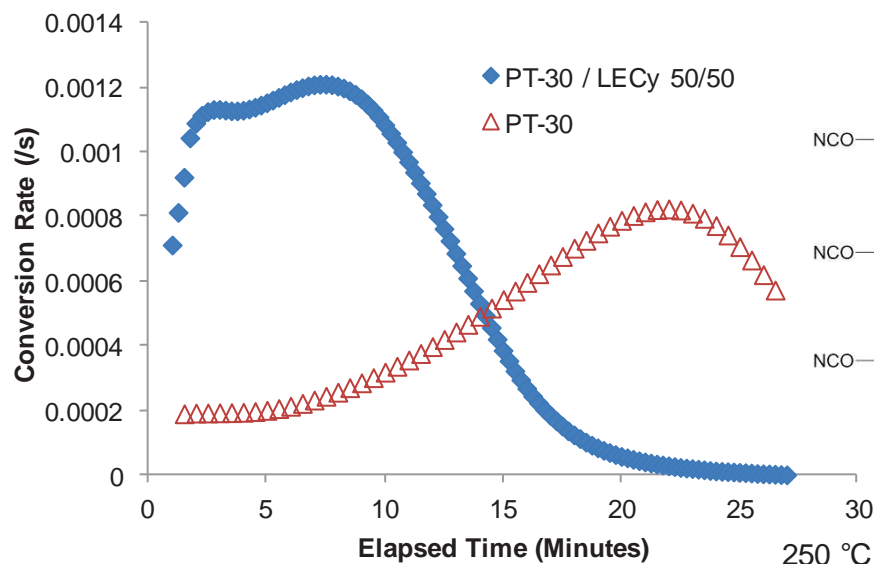
- If the T_G at full cure matches the maximum T_G attainable under a given set of process and catalyst constraints, then no part of the T_G envelope is “wasted” and many aspects of long-term performance are maximized



Cyanate Ester Co-Networks (“Blends”)



- **Self-compatibilizing**



- **Synergistic Properties**

- **More gradual cure characteristics**



Measuring Co-Network Synergy

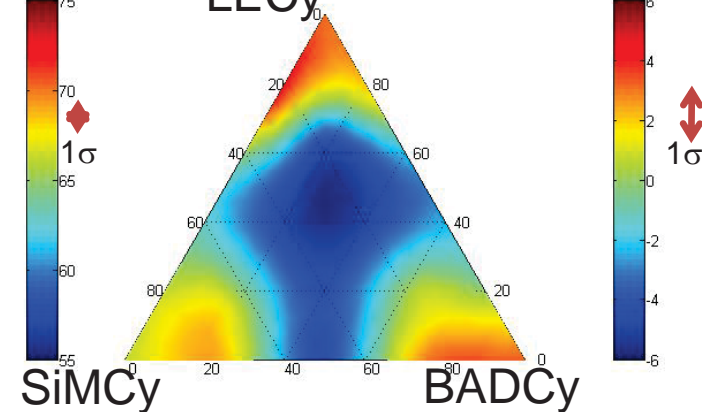
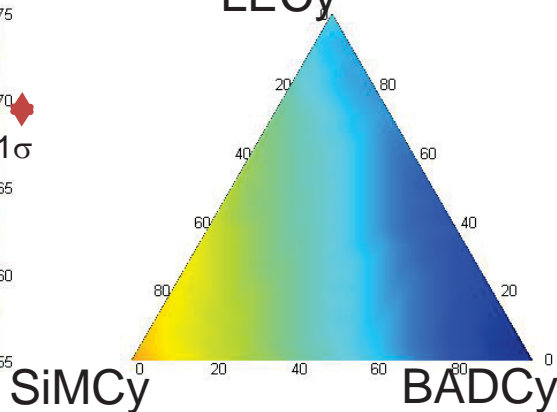
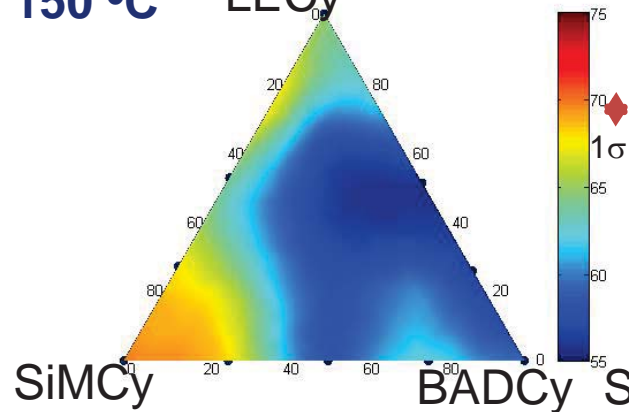


CTE @
150 °C

Absolute
LECy

- Expected
LECy =

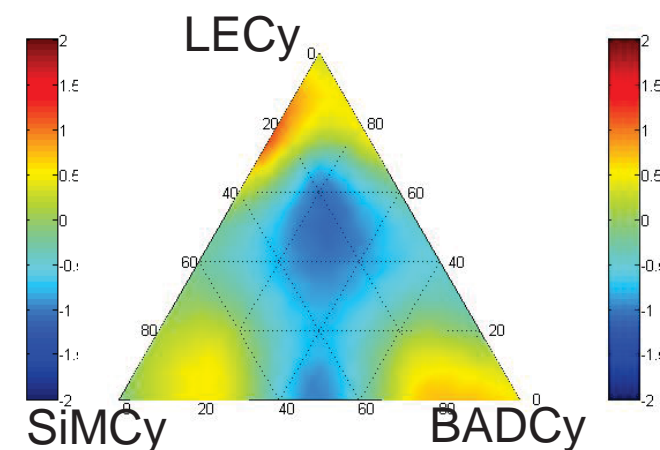
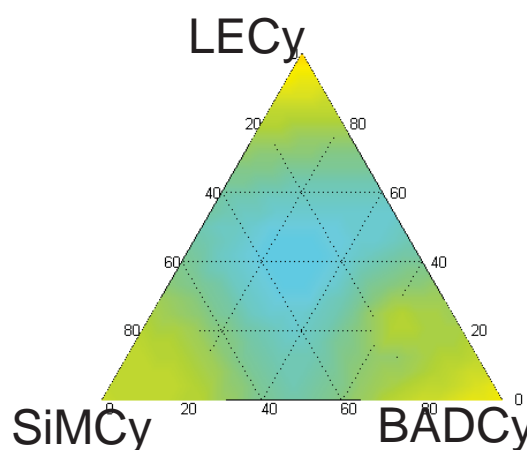
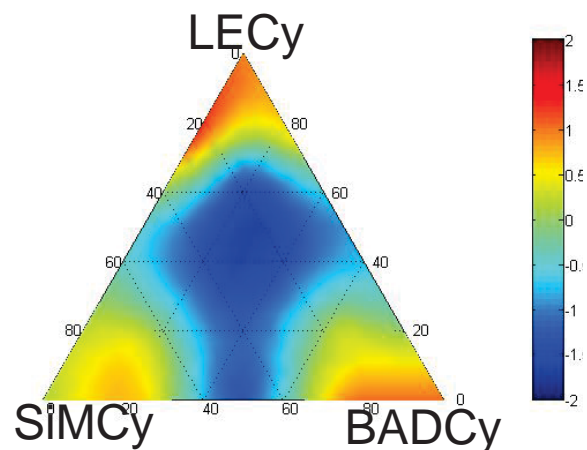
Deviation
LECy



Studentized Residual

= Systematic +

Random Variation



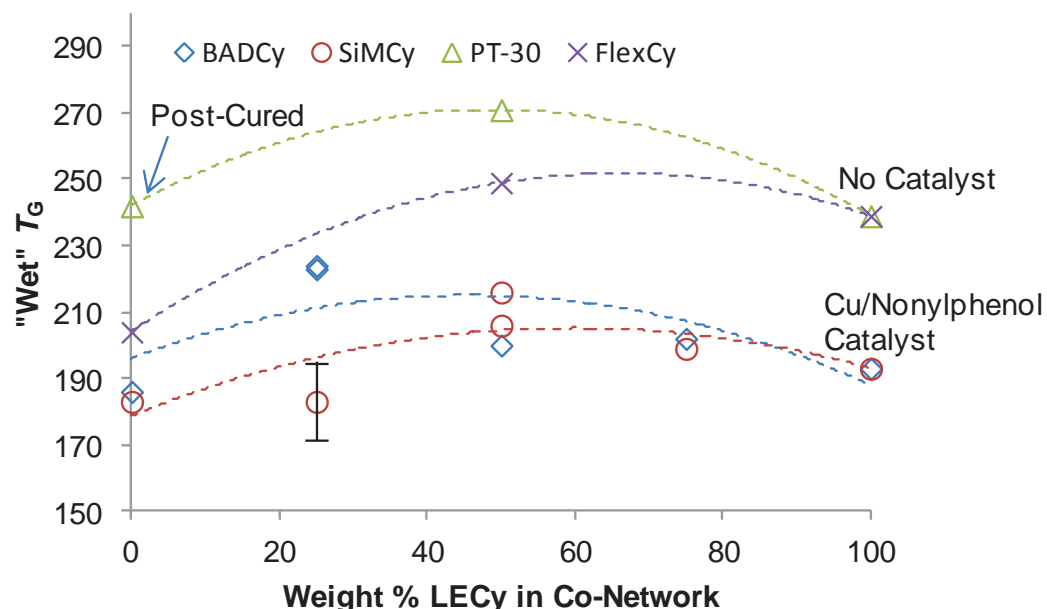
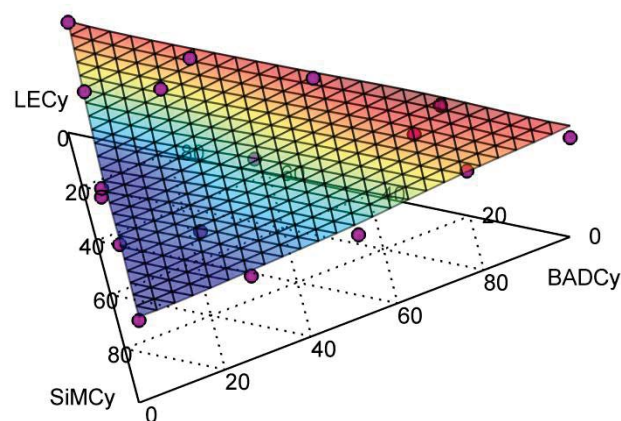
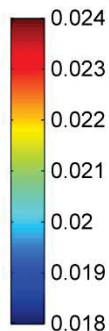
- Systematic patterns identify both general (as in CTE) and pair-specific interactions



Water Uptake and Wet T_g in LECy Co-Networks



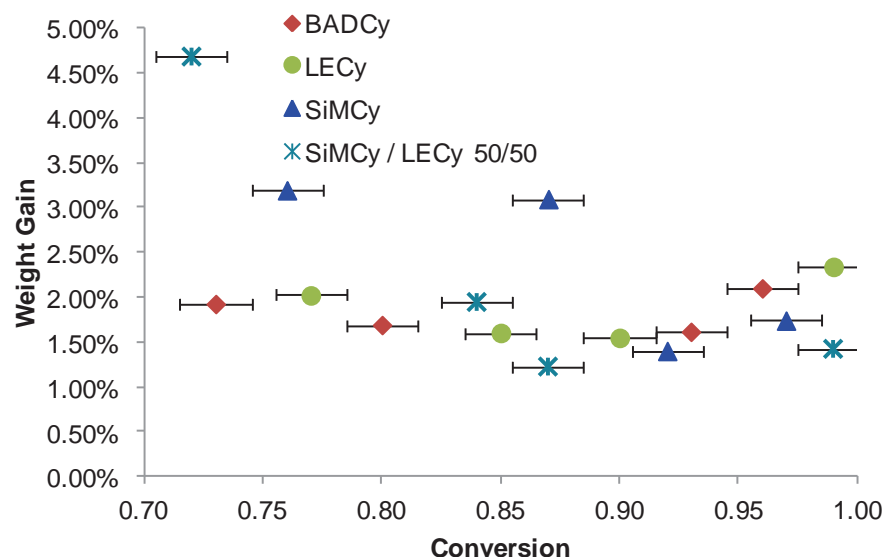
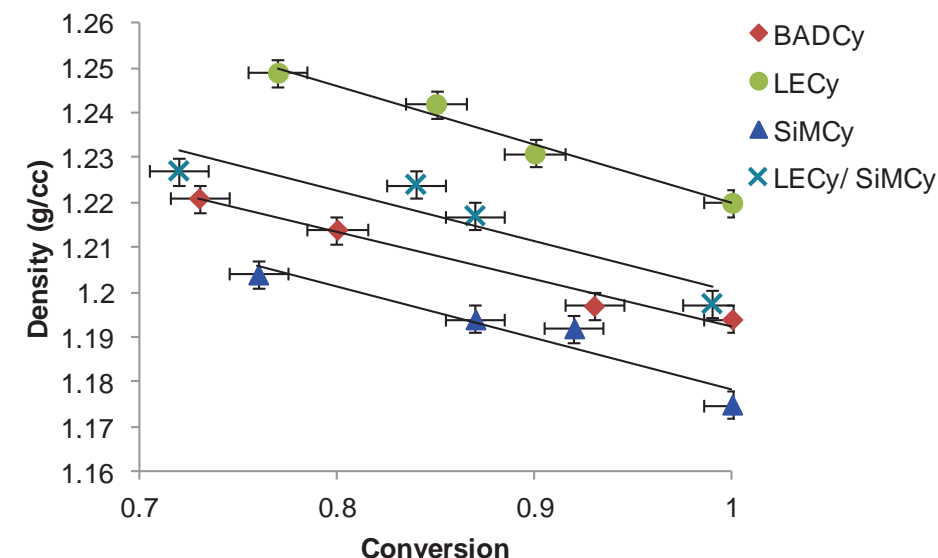
Moisture Uptake (wt. frac.)



- Among cyanate esters studied to date, co-networks with LECy tend to exhibit a lower moisture uptake and a higher wet T_g than would be predicted by a rule of mixtures
- The T_g increase appears to be a consistent synergistic effect with a magnitude of 15-40 °C depending on resin and catalyst type
- The degree of cure and of degradation in these “wet” samples has not yet been determined



Role of Co-Network Formation in Moisture Uptake



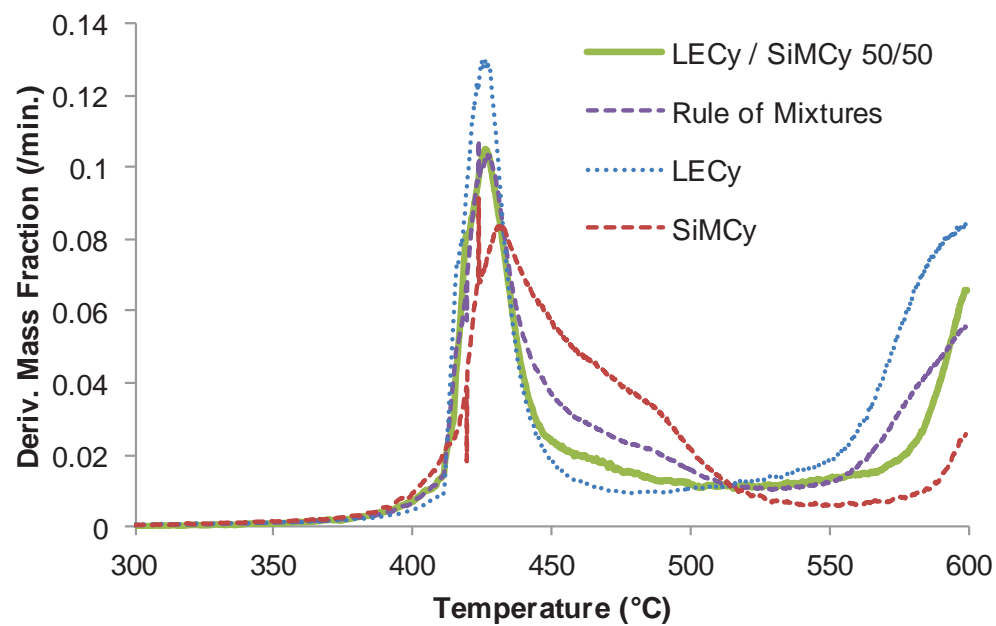
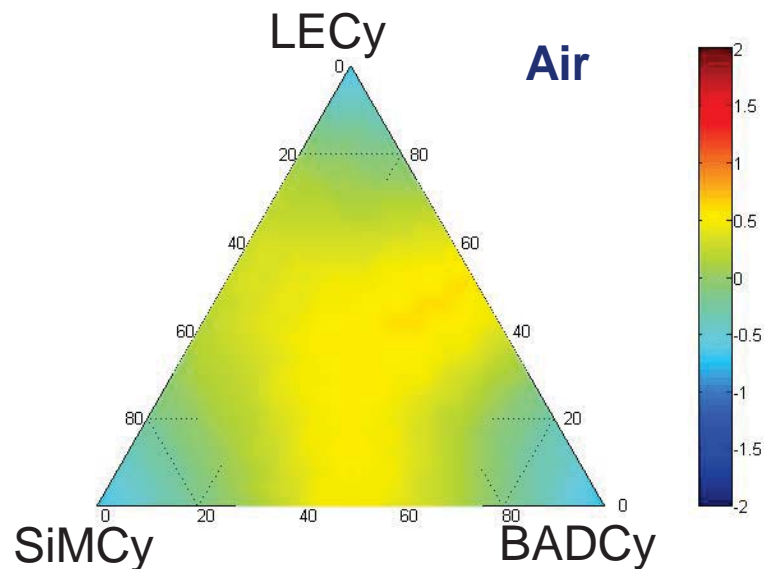
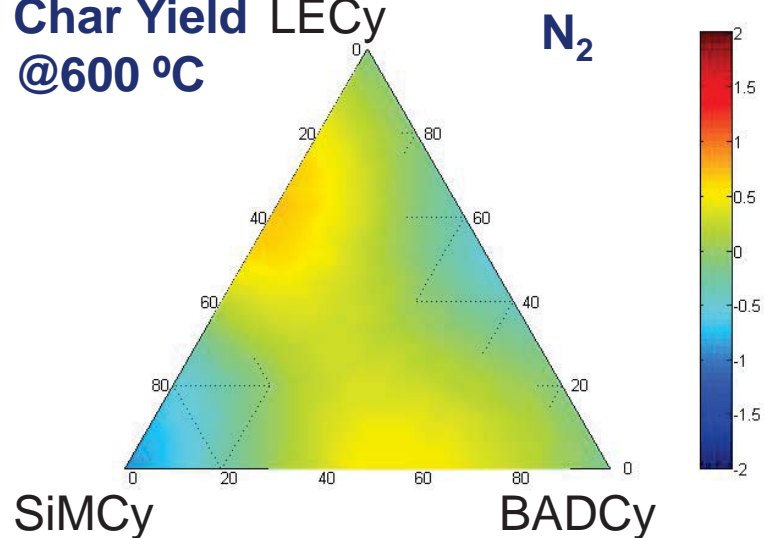
- Post-vitrification, the formation of one mole of cyanurate groups “locks in” about 35 cc of free volume
- Above about 85% conversion, the extra free volume has been shown to possess dimensions capable of accommodating water
- Water uptake in cyanurate networks is minimized at 85-90% conversion, perhaps due to the competing effects of “loose ends” and cyanurate free volume formation
- The amount of “extra” moisture absorbed at high conversions appears to vary considerably with monomer structure, with the SiMCy/LECy blend showing a very small increase



Char Yields in Cyanate Ester Co-Networks



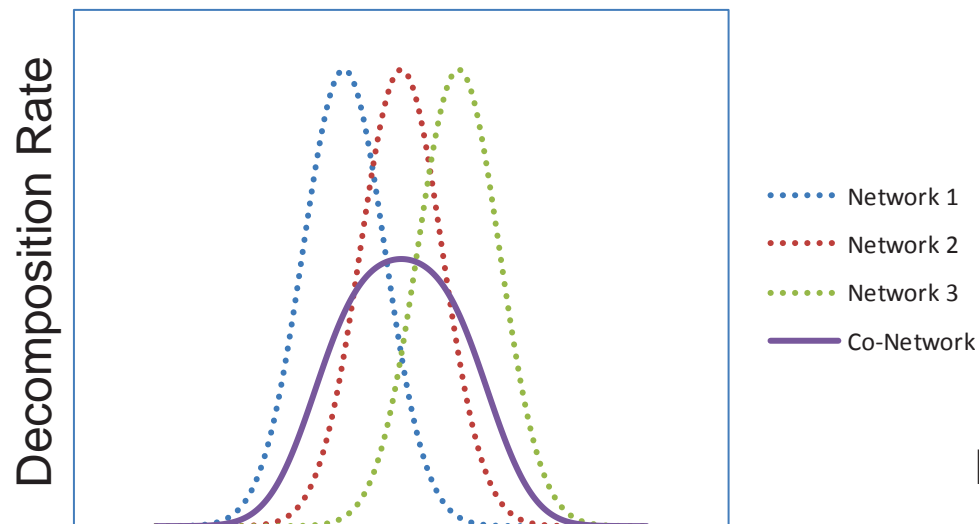
Char Yield LECy
@600 °C



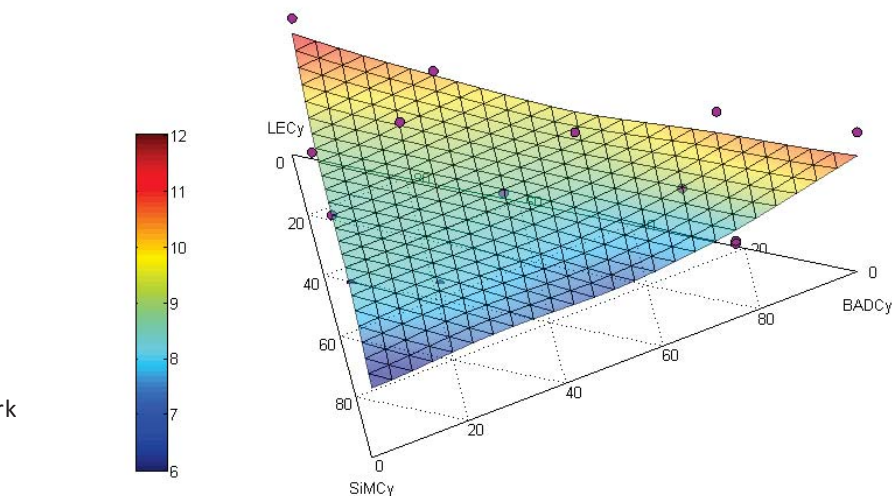
- Strong synergistic effects were not observed for the char yields of di(cyanate ester) blends in either N_2 or air. Though some secondary effects may increase char yields, the mechanism for these is unknown.



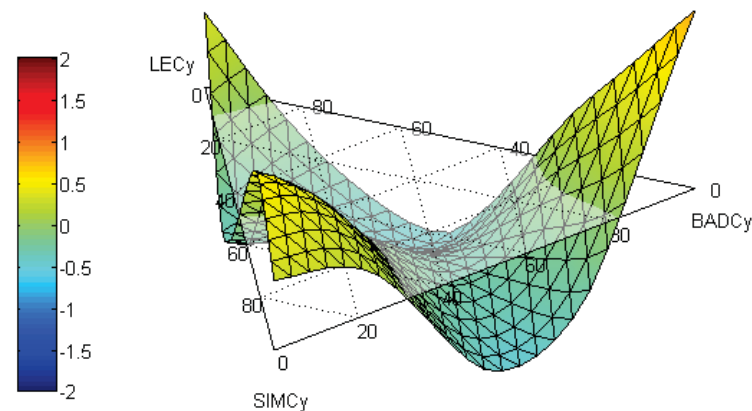
Thermal Degradation in Cyanate Ester Co-Networks



- Because different network components decompose at slightly different temperatures, the overall decomposition of the network is more gradual, thereby reducing the maximum mass loss (and possibly heat release) rate.



Maximum decomposition rate in nitrogen



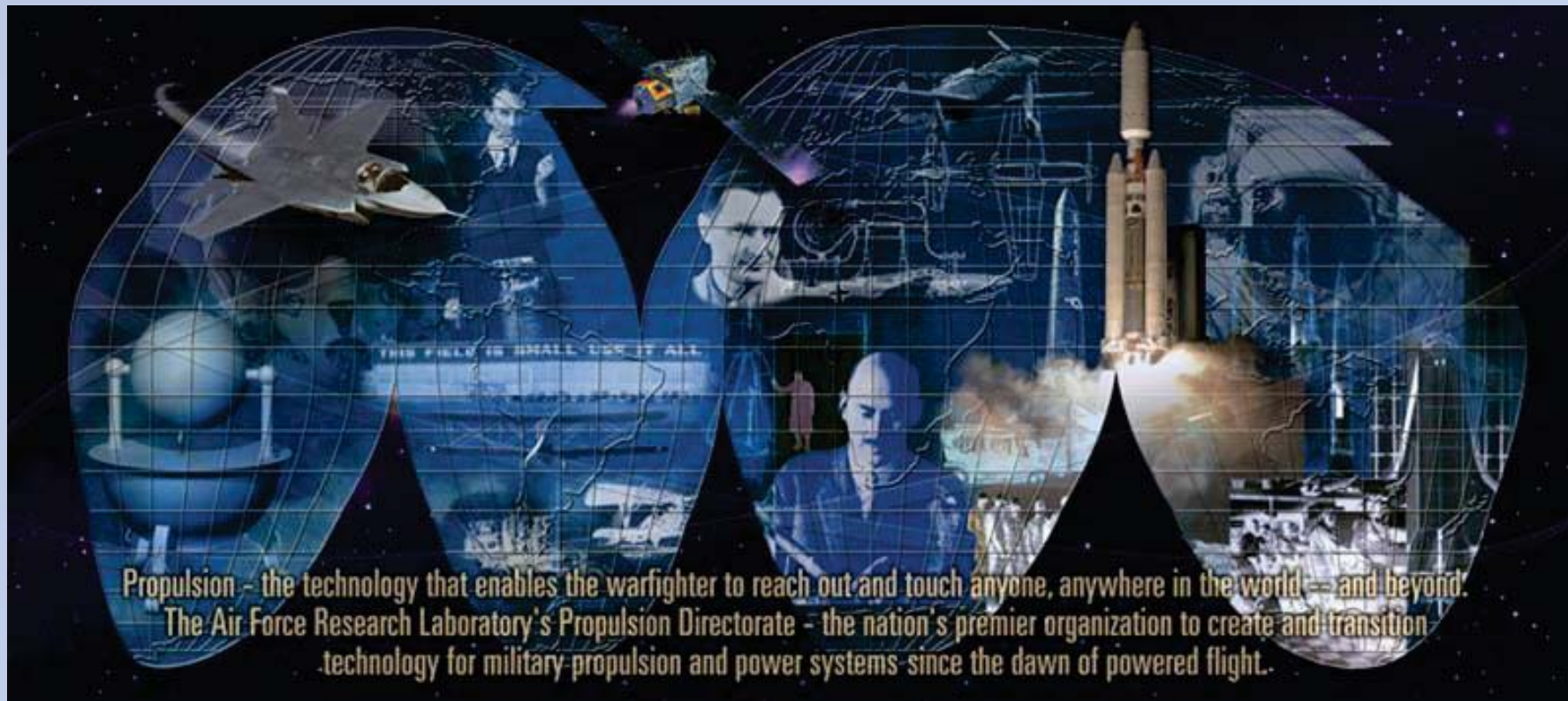
Systematic deviation from rule of mixtures

From Guenthner et al. *Macromolecules* **2012**, 45, 211-220



Summary

- The attainable T_G in a cyanate ester thermosetting resin is not a fixed quantity but varies over an envelope determined by the degree of conversion and the limits of mechanical and chemical stability of the cure network
- The short-term chemical stability of cyanurate networks appears to be optimal when segments and junctions containing tertiary or quaternary carbons are avoided (based solely on empirical observation)
- Using combinations of methylene and phenylene junctions and spacers in cyanurate networks, the T_G -conversion characteristics can be tuned to match processing constraints without sacrificing thermochemical stability
- In addition to network architecture, the formation of co-networks can improve aspects of thermo-mechanical and thermo-chemical stability; in particular, better resistance to wet environments appears to be a general characteristic of co-networks incorporating LECy
- Co-networks with thermochemically dissimilar components enable phased degradation that reduces maximum mass loss rates



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